Bilayer CoO_x-TiO_2 mesoporous-photonic crystal films for visible light harvesting and photocatalysis

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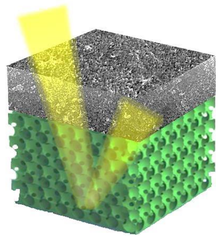
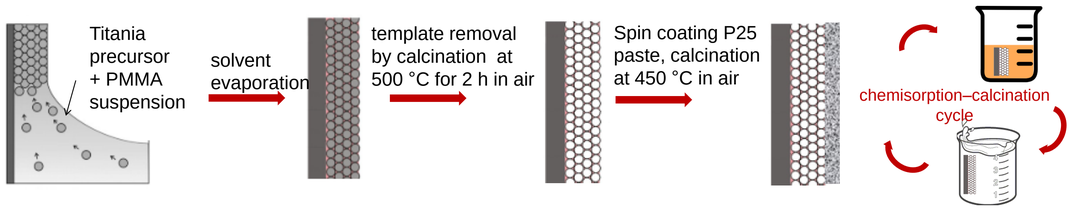
Photonic crystal assisted TiO_2 photocatalysis

An advanced photon management approach that aims at enhancing titania's ability to harness solar light is by structuring TiO_2 photocatalysts in the form of photonic crystals [1]. This modification combines the unique potential for slow photon-assisted light harvesting, mass transport and adsorption of macroporous periodic structures such as inverse opals with compositional tuning of the catalysts for enhanced charge separation and visible light activation (VLA). However, besides single layer inverse opals, application of complex architectures such as multilayer stacks of 3D photonic crystals in photocatalysis remains essentially unexplored [2]. This work reports the deposition of heterostructured films consisting of a TiO_2 inverse opal bottom layer and a highly efficient mesoporous titania top layer using the benchmark Aeroxide® P25 (Evonik) titania nanopowder, modified by "molecular" scale CoO_x nanoclusters using the chemisorption-calcination-cycle (CCC) method [3], in order to enhance visible light harvesting and photocatalytic activity by means of slow photons and Bragg reflection.



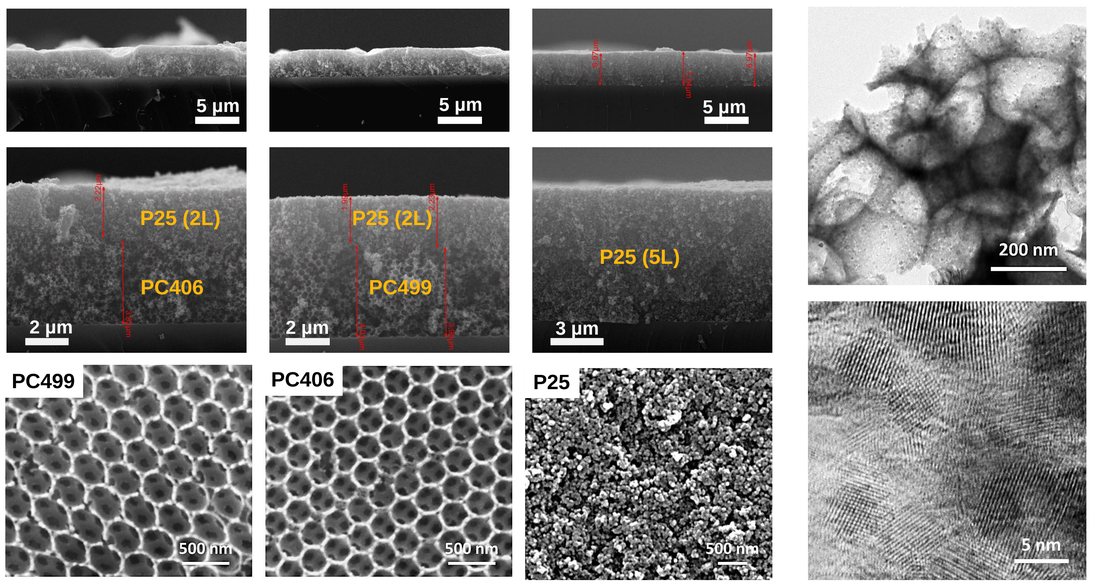
Bilayer fabrication and CoO_x surface modification

Well-ordered photonic band gap engineered anatase TiO_2 inverse opal underlayers were deposited using the evaporation-induced co-assembly of PMMA colloidal spheres of 406 and 499 nm diameters with a hydrolyzed Ti alkoxide precursor. Cleaned glass slides were vertically suspended in a vial containing 20 ml of 0.125 wt% diluted PMMA sphere suspension in Milli-Q water and 0.14 ml of fresh titania precursor (1.25 ml TiBALDH solution, 0.5 ml HCl 0.1 M and 1 ml EtOH), both sonicated for 30 min prior to use. The vials with the suspended glass substrates were kept at 55 °C until the solvent fully evaporated over a period of 3 days, yielding composite films comprising the titania gel distributed within the interstices of the close packed PMMA opal structure. The dry films were then calcined at 500 °C for 2 h in air at a heating rate of 1 °C/min, to remove the polymer matrix and crystallize titania in the inverse opal structure.



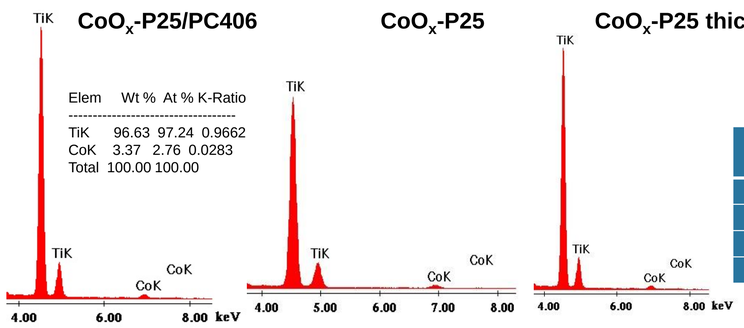
Mesoporous TiO_2 layers (2 and 5 L) were deposited on top of the photonic underlayer using a paste of the benchmark Aeroxide® P25 (Evonik) titania nanopowder, by spin coating leading to bilayer films with smooth interfaces. Co oxide modification was performed by immersing the films to 100 ml of 10^{-3} M $Co(acac)_2(H_2O)_2$ solution for 24 h. The films were repeatedly washed with the solvent for the physisorbed complexes to be removed and dried, followed by heating in air at 500 °C for 1 h.

Morphology and surface characteristics



SEM images verified the formation of highly ordered 3D close packed inverse opal structures corresponding to the (111) planes of an *fcc* lattice consisting of void spheres (diameter of 260 nm for PC406 and 310 nm for PC499) within the titania framework. Cross section images disclose a smooth interface between the photonic crystal and the mesoporous P25 top layer. The inverse opal macropores were well interconnected through smaller ones of 50-90 nm (dark circular areas). TEM images reveals that the skeleton consists of ~10 nm nanoparticles with distinct *d*-spacings, the most common being 0.35 nm corresponding to the (101) planes of the anatase TiO_2 phase.

CoO_x surface modification EF-TEM, EDX



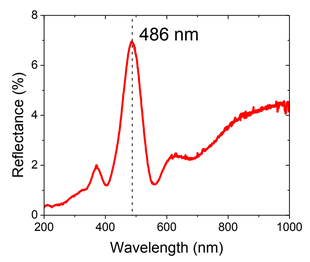
EDX

	Ti at %	Co at %	Ratio
CoO_x-P25/PC406	97,24	2,76	0,028
CoO_x-P25/PC499	97,60	2,40	0,025
CoO_x-P25 (2L)	97,29	2,71	0,028
CoO_x-P25 (5L)	97,22	2,78	0,029

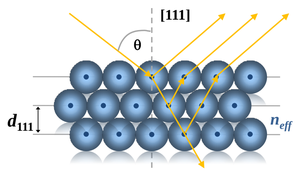
EDX analysis verified the successful deposition of Co species on the bilayer titania films by 1 cycle of the chemisorption-calcination method. The atomic Co percentage was found to be ~2.75%.

Optical properties - PBG engineering vs Visible light activation

Stop bands determination by 15° specular reflectance

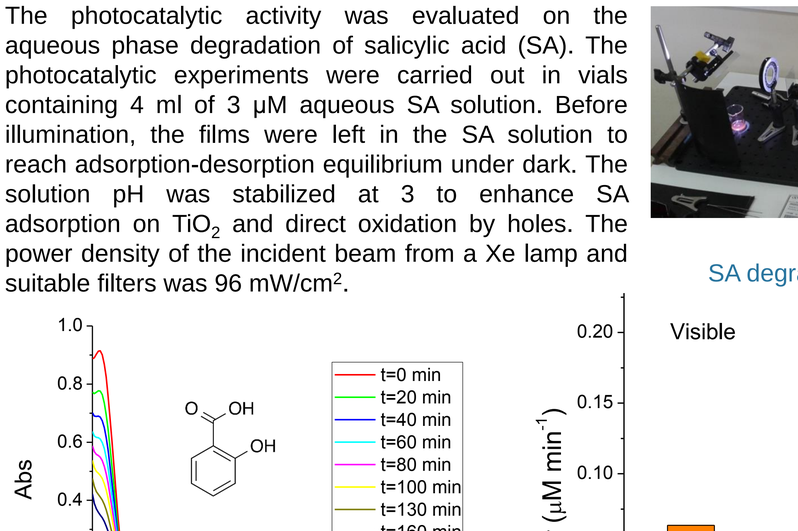


Bragg diffraction



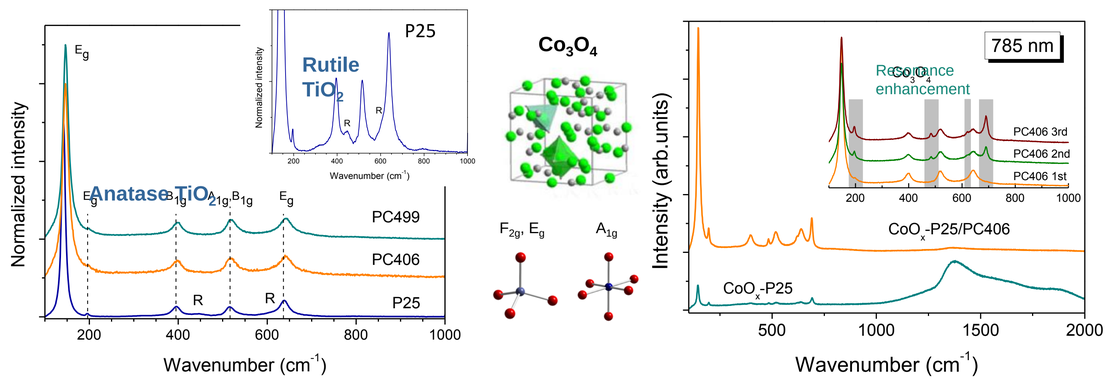
	D (nm)	λ (15°) (nm)	n_{eff}	f	n_{eff} (H_2O)	λ (0°) (air)	λ (0°) (H_2O)
PC406	260	486	1,17	0,069	1,45	498	614
PC499	310	578	1,17	0,067	1,44	593	731

D = macropore diameter of the TiO_2 inverse opal films determined by SEM.
$\lambda_{exp}(15^0)$ = stop band wavelength determined from the 15° incidence specular spectra.
λ (0°) = stop band wavelength predicted from modified Bragg law $\lambda = 2d_{111}\sqrt{n^2_{eff} - sin^2\theta}$,
$n^2_{eff} = n^2_{sphere} f + n^2_{solid}(1\text{-}f)$ for θ=0° incidence angle and $d_{111} = \sqrt{2/3}D$ the spacing of (111) planes.



Increase of diffuse reflectance and shift of TiO_2 electronic absorption edge (rutille phase) after the deposition of the P25 layer. CoO_x deposition leads to local DR% minima at 420 and 700 nm caused by the visible light absorption bands of Co oxides, particularly the d-d transitions of Co_3O_4 spinel.

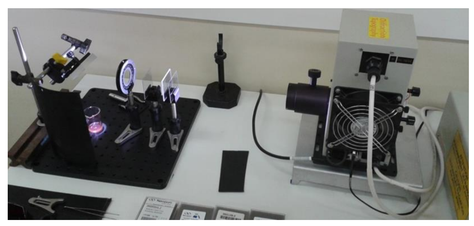
Raman spectroscopy – identification of Co oxides



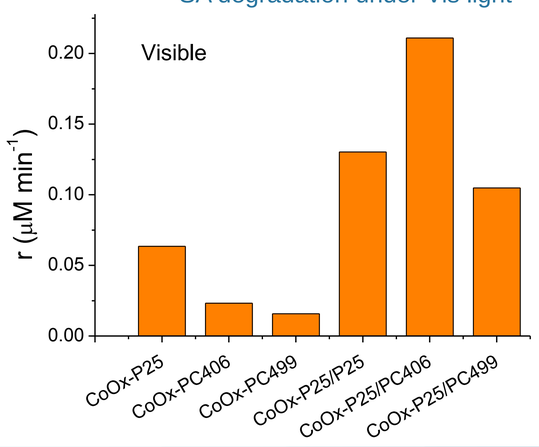
Vibrations at 194, 482 και 691 cm^{-1} arise from the F_{2g}, E_g and A_{1g} modes of the tetrahedral (CoO_4) and octahedral (CoO_6) units in the $Co_3O_4 = [Co^{2+}][Co^{3+}]_2[O^{2-}]_4$ normal spinel. In defect-free CoO, first-order Raman scattering is forbidden due to its centrosymmetric cubic NaCl-type structure. The higher intensity of the Co_3O_4 Raman bands at 785 nm is due to the optical absorption and the consequent resonant enhancement of Raman scattering by the surface Co-oxides.

Photocatalytic activity

The photocatalytic activity was evaluated on the aqueous phase degradation of salicylic acid (SA). The photocatalytic experiments were carried out in vials containing 4 ml of 3 μM aqueous SA solution. Before illumination, the films were left in the SA solution to reach adsorption-desorption equilibrium under dark. The solution pH was stabilized at 3 to enhance SA adsorption on TiO_2 and direct oxidation by holes. The power density of the incident beam from a Xe lamp and suitable filters was 96 mW/cm^2.



SA degradation under Vis light



Tuning the photonic properties of the TiO_2 substrates to the visible light electronic absorption of the surface CoO_x oxides resulted in the marked enhancement of the bilayer film photocatalytic activity via the synergy of slow photons and Bragg backscattering, surpassing the benchmark P25 films of higher thickness. The highest performance was achieved in the case of amplification by "red" slow photons of the TiO_2 photonic underlayer in combination with the lesser contribution by Bragg reflection to the nanocrystalline TiO_2 top layer, indicating that photonic crystals can be effective both as photocatalytic layers and Bragg mirrors in heterostructured photocatalytic films.

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[3] Q. Jin, H. Yamamoto, K. Yamamoto, M. Fujishima, H. Tada, Simultaneous induction of high level thermal and visible-light catalytic activities to titanium(IV) oxide by surface with cobalt(III) oxide clusters, Phys. Chem. Chem. Phys. 15, 20313 –20319 (2013).

Acknowledgments
Alexia Toumazatou acknowledges the Onassis Foundation scholarship for doctoral studies. We also acknowledge support for part of this work by the project MIS 5002772, implemented under the Action "Reinforcement of the Research and Innovation Infrastructure", funded by the Operational Programme "Competitiveness, Entrepreneurship and Innovation" (NSRF 2014-2020) and co-financed by Greece and the European Union (European Regional Development Fund)